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Time-Resolved Picosecond Infrared Absorption Induced by High-Density Photogenerated Carriers in Ge and CdSe

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Abstract—**Picosecond time-resolved absorption at 2.2, 3.4, and 3.9 μm produced by photogenerated carriers in intrinsic Ge and semi-insulating CdSe has been measured at room temperature. For Ge, the peak absorbance changes as the square of the probe wavelength. The absorption profile as a function of delay time relative to the excitation pulse rises with a resolution-limited risetime (<10 ps) and decays over the range from several hundred picoseconds to several nanoseconds. These observations can be accounted for by free-carrier absorption and Auger recombination. Intervalence transitions make a small contribution (~ 17 percent) to the induced absorption only at 2.2 μm. For CdSe, the absorption change with time exhibits a more complex profile. Two temporal peaks occur for probing wavelengths at 3.4 and 3.9 μm and three peaks occur at 2.2 μm. The first peak occurring at about 5 ps after excitation for all three probe wavelengths with a resolution-limited risetime is due to free-carrier absorption. The other peaks have been attributed to transitions involving impurity (defect) levels by trapped photogenerated carriers.**

INTRODUCTION

OVER the past decade, direct information on the temporal behavior of hot carriers in many semiconductors has been provided from studies of the time-resolved optical spectra of high-density electron–hole plasmas photogenerated by intense ultrashort laser pulses. Such investigations have been accomplished on Ge [1], [2], GaAs [3]–[5], GaSe [6], [7], CdSe [8]–[10], CdS [9], and most recently on microstructures consisting of GaAs-AlGaAs multiple quantum wells [11]–[13]. Previous research on Ge and CdSe related to the present work will be briefly described next.

In the picosecond absorption studies on Ge, the samples were mainly excited by a 1.06 μm pulse, and the transmission of a weak time-delayed probe pulse was followed in time at 1.06 μm [2] and at 1.55 μm [1], [2]. The transmission of the 1.06 μm probe was substantially increased due to the saturation of the optically coupled states [2], [14]. However, in the case of the 1.55 μm probe, the absorption increased after 1.06 μm excitation with a pulse-limited risetime and then decreased with decay times varying from 250 to 450 ps, depending on the excitation intensity [1], [2]. This induced absorption was attributed to a combination of free-carrier [1], [2], intervalence band [2], and Coulomb-assisted indirect absorption [2]. The absorption decay was explained by Auger recombination of the photogenerated carriers [1], [2].

Studies on CdSe particularly relevant to our work have been recent measurements of the time-resolved luminescence in CdSe [8], [10]. Tanaka *et al.* [9] found that the luminescence spectra at 4.2 K has two components corresponding to transitions to the upper two valence states. They obtained a relaxation time of 30 ps for electrons in the upper valence band and a radiative lifetime of 300 ps. Junnarkar [10] obtained luminescence decays of $\sim$35–100 and $\sim$230 ps at 300 K which were attributed to Auger and radiative processes, respectively.

In this paper, the following three objectives have been achieved: the measurement of the energy relaxation of photogenerated hot carriers in intrinsic Ge and semi-insulating CdSe, the identification of some of the transitions involved in the photoexcitation and relaxation of the electrons and holes, and the proposal of mechanisms for explaining some of these processes.

The hot photogenerated carriers were produced by excitation of the samples by $\sim$7 ps pulses of 1.054 μm radiation. For Ge, the photoexcitation was by a single-photon process since its bandgap (0.83 eV) at $k = 0$ is smaller than the incident photon energy (1.19 eV). For CdSe, with a bandgap of 1.73 eV, the hot carriers are generated by a two-photon process. The kinetics of the photogenerated carriers was obtained from the absorption of the infrared (IR) probe pulse as a function of its time delay relative to that of the excitation pulse. The probe beam consisted of a $\sim$5 ps pulse at wavelengths (λ_p) of 2.2, 3.4, and 3.9 μm. At these wavelengths, indirect valence band (V) to conduction band (C) transitions are eliminated in Ge, and the contributions of intervalence transitions can be separated from free-carrier absorption in Ge and CdSe. In addition, time-resolved induced absorption between 2.2 and 3.9 μm should be useful in identifying contributions from impurity and defect levels in CdSe.

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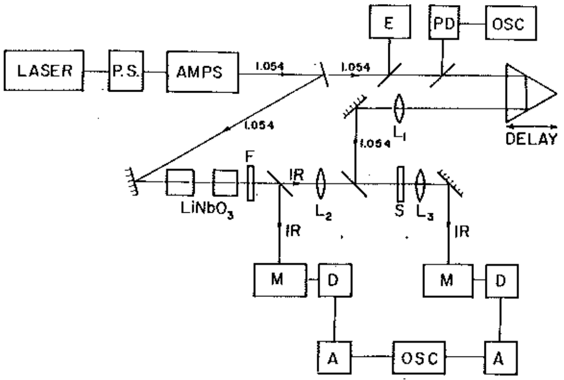

Fig. 1. Experimental setup for picosecond pump and probe measurements. *P.S.* (pulse selector), *E* (energy meter), *PD* (photodiode), *F* (filter), L_1 (30 cm lens), L_2 (10 cm CaF$_2$ lens), L_3 (15 cm CaF$_2$ lens), *S* (sample), *M* (IR monochromator), *D* (IR InSb detector), and *A* (wide-band preamplifier).

EXPERIMENTAL SETUP

The experimental setup is shown in Fig. 1. A mode-locked Nd:glass laser with three amplifiers produces single-mode vertically polarized 1.054 μm pulses of ~ 7 ps and 50 mJ. The output was split into two beams. The first is used for excitation, delivering 150–300 μJ to a ~ 1.5–2 mm spot on the sample after passing through a variable delay prism. The second beam, 90 percent of the laser output, was directed through two 3 cm LiNbO$_3$ crystals to generate a horizontally polarized IR probe beam tunable from 2 to 5 μm [15]. The probe pulse of ~ 30 μJ energy and ~ 5 ps duration was focused to a ~ 0.5 mm diameter spot centered within the larger excitation area on the samples. Both a fraction (f) of the incident IR intensity and that transmitted by the samples were collected by two Perkin Elmer model 1B monochromators equipped with cooled (77 K) Infrared Associates InSb detectors. The two outputs were amplified ($\times 10$) by wide-band preamplifiers and displayed on a Tektronix 7844 dual beam oscilloscope.

The change in transmission ΔT is calculated from the ratio of these two IR signals with the sample excited by 1.054 μm divided by this ratio without excitation. The change in percent transmission for a particular delay time is given by the following equation:

$$\Delta T = \left[\frac{(T)_{\text{IR}}}{f(I)_{\text{IR}}}\right]_p \bigg/ \left[\frac{(T)_{\text{IR}}}{f(I)_{\text{IR}}}\right]_o \tag{1}$$

where ΔT = change in transmitted IR, I = incident IR, T = transmitted IR, f is fraction of incident IR, and p and o refer to the measurements with and without 1.054 μm excitation, respectively. The data from 10–15 laser shots were averaged for each delay time. The 1.054 μm excitation energy (E) was measured by a Laser Precision Corporation energy meter, and the monitoring of the number of laser pulses per shot was done by an S-1 Hamamatsu photodiode (PD) whose output was displayed on a Tektronix 519. In the case of CdSe, a measurement was also made of the 1.054 μm transmission as a function of its incident intensity. To do this, the energy meter was placed ~ 2 cm behind the sample and the IR probe beam was blocked.

SAMPLES

The p-type Ge sample was 1 mm thick, polished on both sides of $\langle 111 \rangle$ orientation with an impurity concentration of $\sim 10^{16}/\text{cm}^3$. The two semi-insulating CdSe crystals of wurtzite symmetry and 1.5 mm thickness were vapor grown and Se annealed. One had its *c* axis perpendicular to its plane, and the other had its *c* axis in the plane and parallel to the long edge (vertical). Unless noted otherwise, the measurements are on the latter CdSe sample.

RESULTS

A. Ge

The absorption of Ge at 2.2, 3.4, and 3.9 μm as a function of delay time between the probe and pump pulses is displayed in Fig. 2. From the temporal behavior, one finds that the risetime is resolution limited (< 10 ps). The decay time, because of the large standard deviations in the data, is estimated to have a range from ~ 200 ps to several nanoseconds. The maximum values of the induced absorbances are 0.15 ± 0.03, 0.31 ± 0.06, and 0.60 ± 0.14 for the probe wavelengths of 2.2, 3.4, and 3.9 μm, respectively. These results are plotted in Fig. 3; within experimental error, they are proportional to λ_p^2, which is indicative of free-carrier absorption [16]. The induced absorbances also increased linearly with the intensity of the 1.054 μm excitation until they saturated at an intensity of $\sim 2.0 \times 10^{16}$ photons/cm^2.

B. CdSe

The temporal behavior of the induced absorbance for CdSe shown in Fig. 4 is more complex. For all three probe wavelengths, there are peaks at ~ 5 and ~ 192 ps, with an additional peak at ~ 20 ps appearing for the 2.2 μm probe. The 5 ps peak at 2.2 μm appears real since it was consistently observed in two separate experiments with 12–15 shots for each of the three delay time points defining it. The 5 ps peak is characterized by a resolution-limited (< 10 ps) risetime and decay times shorter than 50 ps. Its maximum values of optical density are 0.067 ± 0.025, 0.14 ± 0.07, and 0.16 ± 0.05 for $\lambda_p = 2.2, 3.4$, and 3.9 μm, respectively. If this peak were due to free-carrier absorption ($OD \propto \lambda_p^2$), then these values (normalized to 0.067 at 2.2 μm) would be 0.16 and 0.21 for $\lambda_p = 3.4$ and 3.9 μm, respectively. Within experimental error, the λ_p^2 behavior is fulfilled. Although for the 2.2 μm probe the risetimes of the 192 and 20 ps peaks are defined by only two data points [see Fig. 4(c)], the latter were determined by 12–15 laser shots on several experimental runs. Consequently, we believe that these peaks are real, but because of the large fluctuations in the data, their risetimes and decay times are poorly defined. The induced IR absorbances of the peaks at 5 and 192 ps were independent of excitation intensity over the range of 10^{14}–3×10^{15} photons. The optical density at the excitation

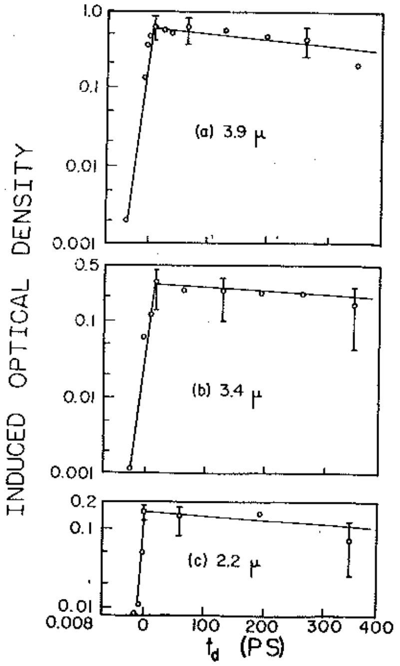

Fig. 2. Time-resolved induced absorption for 1 mm thick Ge at 295 K. (a) 3.9 μm probe, (b) 3.4 μm probe, and (c) 2.2 μm probe. Circles are experimental points. Error bars indicate standard deviations. The risetimes τ_r are <10 ps. The decay times τ_d can fit 200 ps to several ns for all cases.

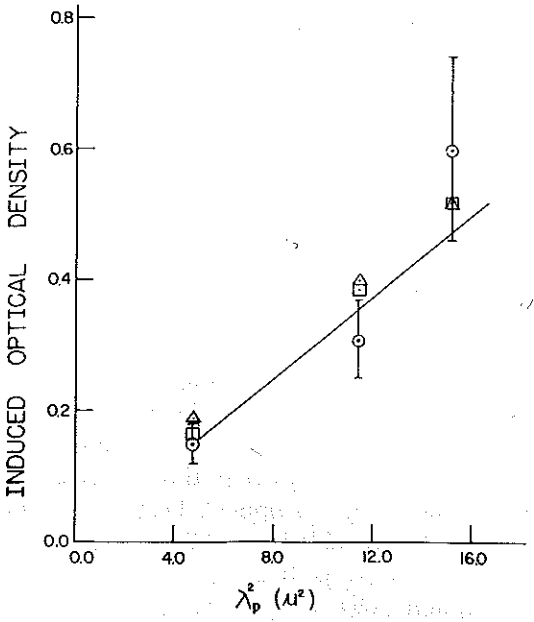

Fig. 3. The maximum induced absorption for Ge as a function of the square of the probe wavelength (λ_p^2). Circles are experimental points with error bars indicating standard deviations, squares give the calculated values for free-carrier absorption from Table I, and triangles refer to the sum of the calculated values for free-carrier and intervalence absorption from Tables I and II. The line corresponds to $OD \propto \lambda_p^2$.

wavelength of 1.054 μm was found to be 0.3 after correction for reflection losses and was also independent of the pump intensity. The time-resolved absorption at 3.4 μm for the sample whose c axis is perpendicular to the face gave similar results to that shown in Fig. 4(b) for the sample with its c axis parallel to the face.

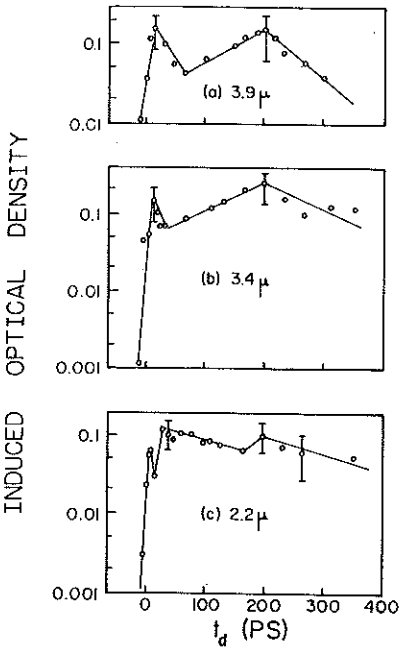

Fig. 4. Time-resolved induced absorption for 1.5 mm thick CdSe at 295 K. (a) $\lambda_p = 3.9$ μm, (b) $\lambda_p = 3.4$ μm, (c) $\lambda_p = 2.2$ μm. Circles are experimental points. Error bars indicate standard deviations. The risetimes of the first peak are <10 ps.

DISCUSSION

A. Ge

The induced absorption at 2.2, 3.4, and 3.9 μm appears to be due principally to photogenerated free carriers with varying degrees of contributions from intervalence band transitions depending on λ_p. Auston originally suggested the former to explain the 1.55 μm absorption induced by 1.06 μm excitation [1], although Smirl [2] indicated that contributions from intervalence and indirect ($V \rightarrow C$) absorption must also be included for $\lambda_p = 1.55$ μm. However, at the probe wavelengths used in our study, namely, 2.2 μm (0.57 eV), 3.4 μm (0.37 eV), and 3.9 μm (0.32 eV), indirect absorption from the upper bands at $k = 0$ to the lowest energy conduction band at the L symmetry point is not possible since the indirect bandgap is 0.67 eV. Intervalence probe absorption between valence bands $2 \rightarrow 1$ and $3 \rightarrow 2$ (Fig. 5) is also not possible since this would require probe energies <0.30 eV.

Transitions between bands $3 \rightarrow 1$ are allowed for some of the probe wavelengths and will be discussed in this section. We will calculate the contributions from both free-carrier and intervalence absorption induced by 1.054 μm excitation. The induced free-carrier absorption coefficient is given by

$$\Delta\alpha_c(\text{cm}^{-1}) = \sigma_e N_e + \sigma_h N_h \tag{2}$$

where the σ's refer to the cross sections (cm^2) and the N's to the photogenerated carrier densities (cm^{-3}) for electrons (e) and holes (h). From the known values of $\sigma_e = 4 \times 10^{-18}$ cm^2 and $\sigma_h = 3.3 \times 10^{-17}$ cm^2 at 1.55 μm [1], we obtain the cross sections at our probe wavelengths from their λ^2 dependence [16]. These values of σ, N ($N_e = N_h$

TABLE I

FREE-CARRIER ABSORPTION PARAMETERS AND OPTICAL DENSITIES IN GERMANIUM. $\sigma_{e,h}$ IS THE ELECTRON HOLE CROSS SECTION, $\Delta\alpha_c$ IS THE CALCULATED MAXIMUM INDUCED ABSORPTION COEFFICIENT, N IS THE FREE-CARRIER DENSITY, ΔOD_c IS THE CORRESPONDING CALCULATED INDUCED OPTICAL DENSITY, AND ΔOD_m IS THE MAXIMUM MEASURED INDUCED OPTICAL DENSITY

λ_p (µm)	σ_e (cm^2)	σ_h (cm^2)	N (cm^{-3})	$\Delta\alpha_c$ (cm^{-1})	ΔOD_c	ΔOD_m
2.2	8.1×10^{-18}	6.6×10^{-17}	5×10^{19}	3.7×10^3	0.16 ± 0.04	0.15 ± 0.03
3.4	1.9×10^{-17}	1.6×10^{-16}	5×10^{19}	9.0×10^3	0.39 ± 0.12	0.31 ± 0.06
3.9	2.5×10^{-17}	2.1×10^{-16}	5×10^{19}	1.2×10^4	0.52 ± 0.15	0.60 ± 0.14

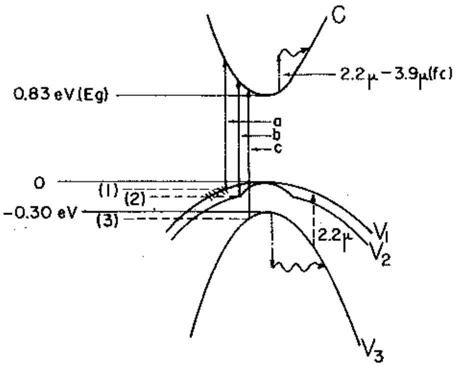

Fig. 5. Band structure near $k = 0$ for Ge. Solid vertical lines indicate 1.054 µm excitation. The single dashed vertical line represents the 2.2 µm probe and the dash–dot, the 2.2 µm → 3.9 µm free-carrier probe (fc), with the wavy line representing phonon absorption and emission. The energies denoted by the dashed horizontal lines are (1) −0.038 eV, (2) −0.14 eV, and (3) −0.32 eV. The effective masses are $m(C) = 0.04\, m_0$, $m(V_1) = 0.34\, m_0$, $m(V_2) = 0.06\, m_0$, and $m(V_3) = 0.075\, m_0$. The slashes on V_1 indicate additional photogenerated holes (see text).

$= N$), the calculated maximum (at saturation) induced absorption coefficients $\Delta\alpha_c$, and the corresponding calculated (ΔOD_c) and measured (ΔOD_m) induced optical densities are listed in Table I. For an intrinsic semiconductor, the number of electrons in a valence band having kinetic energies varying from zero up to a maximum value E is determined by the appropriate total density of states in this band. The incident effective photon density at saturation was $2.0 \pm 0.6 \times 10^{20}/\text{cm}^3$. Due to the rapid randomization of carriers in k space, the maximum carrier density generated by the 1.054 µm pump which is available to absorb the polarized infrared probe is 1/3 of this photon density or $0.67 \pm 0.20 \times 10^{20}/\text{cm}^3$. We will now compare this value to the appropriate total density of states of the three valence bands calculated from (3) [16]:

$$N(V) = 8\pi \sum_{i=1}^{3} \left[2m(V_i)\left|E(V_i)\right|\right]^{3/2} / 3 \tag{3}$$

where $m(V_i)$ is the effective mass for band V_i and $E(V_i)$ is the initial state of excitation relative to the maxima of the valence band (V_i). The values of $E(V_i)$ are obtained from the intersection of the excitation k vectors and the valence bands (see Fig. 5). They are $E(V_1) = -0.038$ eV, $E(V_2) = -0.14$ eV, and $E(V_3) = -0.02$ eV. Substituting these values and the corresponding hole masses $m(V_1) = 0.34\, m_0$, $m(V_2) = 0.06\, m_0$, and $m(V_3) = 0.075\, m_0$ into (3) gives $N(V) = N(V_1) + N(V_2) + N(V_3) = 10^{19}/\text{cm}^3$. Since $\Delta\alpha_c = (\sigma_e + \sigma_h)N$, the calculated values of $\Delta\alpha_c(\text{cm}^{-1})$ are 0.74×10^3, 1.8×10^3, and 2.4×10^3 for $\lambda_p = 2.2$, 3.4, and 3.9 µm, respectively. From Smirl's transmission measurements [2], the absorption coefficient for 1.06 µm radiation is 1.6×10^4 cm^{-1}, giving an effective sample thickness (80 percent absorption) of $t = 1$ µm. Since $\Delta OD = \Delta\alpha t/2.3$, the calculated values of the induced absorbance becomes 0.032, 0.078, and 0.104 for $\lambda_p = 2.2$, 3.4, and 3.9 µm, respectively. These values are smaller than those observed by a factor of five. This indicates that the calculated values of N are too small by this factor. It is reasonable to assume that electrons from V_1 whose energies range from −0.038 to −0.14 eV (slashed region in Fig. 5) can make the transition to band V_2 within the duration of the exciting pulse by carrier–carrier elastic scattering and then be excited to the conduction band. It can be shown, from the equation for density of states previously given, that this process contributes additional carriers with $N = 4 \times 10^{19}/\text{cm}^3$, giving a total value of $5 \times 10^{19}/\text{cm}^3$ for the density number of photogenerated holes (electrons). The resulting calculated values of optical density appear in Table I and compare favorably to the measured values of induced absorbance. This value for the density of photogenerated electrons also agrees within experimental error with the density of exciting photons at which the absorbance saturates, namely, $6.7 \pm 2.0 \times 10^{19}/\text{cm}^3$. Consequently, the observed saturation of absorbance is due to the excitation of all available valence band electrons.

Let us now consider contributions from intervalence absorption. Transitions between the splitoff band V_3 and the light hole band V_2 are only possible for electrons in V_3 with k values between arrows c and b in Fig. 5. This corresponds to probe energies between 0.27 and 0.29 eV which were not accessible in our experiments. However, transitions $V_3 \rightarrow V_1$ are possible for probe wavelengths of 3.4 and 3.9 µm between arrows b and c, as can be seen in Fig. 5. This transition is also possible for the 2.2 µm probe if the electrons in V_1 with energies varying from −0.035 to −0.14 eV (slashed region in Fig. 5) are also excited to the conduction band by the 1.054 µm pump. This reasonable assumption was previously made to give agreement with the measured free-carrier optical densities. Consequently, the transition, $V_3 \rightarrow V_1$ is possible for all three probe wavelengths. The vertical dashed arrow in Fig. 5 represents the 2.2 µm probe. The small density of states of V_3 available for these transitions will be the lim-

TABLE II

INTERVALENCE ($V_3 \rightarrow V_1$) ABSORPTION PARAMETERS AND OPTICAL DENSITIES IN GERMANIUM. ΔE_p IS THE LINEWIDTH OF THE PROBE, E_{pi} IS THE ENERGY OF THE INITIAL PROBE STATE IN V_3, σ IS THE CROSS SECTION, $N(V_3)$ IS THE DENSITY OF AVAILABLE ELECTRONS IN V_3, $\Delta\alpha_c$ IS THE CALCULATED INDUCED ABSORPTION COEFFICIENT AND ΔOD_c IS THE CALCULATED INDUCED OPTICAL DENSITY FOR INTERVALENCE BAND TRANSITIONS

λ_p (μm)	ΔE_p (eV)	E_{pi} (eV)	σ (cm^2)	$N(V_3)$ (cm^{-3})	$\Delta\alpha_c$ (cm^{-1})	ΔOD_c
2.2	0.050	−0.64	0.9×10^{-16}	6.5×10^{18}	580	0.025
3.4	0.008	−0.44	1.5×10^{-16}	1.9×10^{18}	280	0.012
3.9	0.003	−0.32	1.6×10^{-16}	3.0×10^{17}	48	0.002

iting factor in the calculation of induced absorbance. Consequently, $\Delta\alpha(3 \rightarrow 1) = \sigma(3 \rightarrow 1)N(V_3)$ where the cross section $\sigma(3 \rightarrow 1)$ can be obtained from Braunstein [17] and $N(V_3)$ is the appropriate density of states which determines the number of electrons which will absorb photons. This term is the sum of two density of states; one is within the linewidth of the probe, given in Table II, and the other is between the initial state for probe absorption and 0.032 eV above it. It can be shown from the theory of Conwell [18], using the value of 32 meV for the nonpolar LO phonon energy and a deformation potential of 0.7×10^9 eV/cm, that the rate of energy loss by −0.34 eV electrons in V_3 by nonpolar phonon emission is 0.60×10^{10} eV/s. This gives a time of ~5 ps for these electrons to relax by emitting one LO phonon. Consequently, electrons in V_3 with energies up to this value above the initial absorbing state can lose sufficient energy rapidly to be available for absorption by the 5 ps probe. The value of $N(V_3)$ can then be obtained from (3). The appropriate parameters for this calculation as well as the resulting values of the induced intervalence absorbance appear in Table II. A comparison of these results (Table II) to that for free-carrier absorption (Table I) indicates that intervalence absorption is ~17 percent at 2.2 μm. Its contribution at 3.4 μm is ~3 percent and is completely negligible at 3.9 μm. Since the calculated induced absorbance at 2.2 μm due to both free-carrier and intervalence processes (0.18) is greater than that observed (0.15) (see Tables I and II), both may be partially contributing with the dominant contribution due to free-carrier absorption. On the other hand, since the intervalence contributions are smaller than the experimental errors, they may not contribute at all.

The observation of risetimes on the order of the convolution of the pump and probe pulses (< 10 ps) indicates that the induced absorption most likely starts from the terminal excitation states, which also agrees with a free-carrier absorption process. The decay times could not be accurately obtained due to the large fluctuations in the data. Estimated values can range from several hundred picoseconds to nanoseconds. These decay times are in the domain of Auger recombination lifetimes. The Auger decay time is given by the expression $\tau_A = 3/\gamma N_e^2$ where $\gamma = 1.1 \times 10^{-31}$ [1] and $N_e = 5 \times 10^{19}/\text{cm}^3$ (Table I). This yields the value $\tau_A = 10$ ns, which falls into the range of our data.

B. CdSe

Since the first peak at ~5 ps has a convolution-limited risetime and its peak absorbance varies as λ_p^2, it appears to be due to free-carrier absorption. Since there is only one value of σ available in the literature, namely, $\sigma = 2.6 \times 10^{-18}$ cm^2 (1.06 μm) [19], (2) becomes $\Delta\alpha_c = 2\sigma N_{e,h}$. At the maximum excitation intensity, the measured absorbance at 1.054 μm was 0.3, corresponding to 50 percent absorption of the incident intensity of 1.3×10^{15} photons. Since two photons are needed to produce one electron–hole pair, this creates 3.2×10^{14} pairs. As in the case of Ge, due to the rapid randomization of carriers in k space and the polarization of the probe beam, only 1/3 of the generated carriers are available for probe absorption, namely 1.1×10^{14}. For our 1.5 mm beam diameter, this gives $N_{e,h} = 3.3 \times 10^{16}/\text{cm}^3$. Because the relevant density of valence band states $9 \times 10^{19}/\text{cm}^3$ calculated from (3) is, in contrast to Ge, much larger than the electron–hole pair density, the *latter* density, $3.3 \times 10^{16}/\text{cm}^3$, is the appropriate quantity to be used for $N_{e,h}$. Adjusting the published value of σ at 1.06 μm for λ_p using the appropriate λ^2 correction, as was done for Ge, gives free-carrier cross sections of 1.1×10^{-17}, 2.7×10^{-17}, and 3.6×10^{-17} cm^2 for λ_p = 2.2, 3.4, and 3.9 μm, respectively. Since $N_{e,h} = 3.3 \times 10^{16}/\text{cm}^3$, the corresponding calculated values of $\Delta\alpha_c$ are 0.73, 1.8, and 2.4 cm^{-1}. For the sample thickness of 0.15 cm, this yields induced optical densities of 0.05, 0.12, and 0.16 for λ_p = 2.2, 3.4, and 3.9 μm, respectively. These agree within experimental error with the corresponding measured values of 0.067 ± 0.025, 0.14 ± 0.07, and 0.16 ± 0.05. Recent observations of self-defocusing in CdSe with two-photon excitation [20] could decrease $N_{e,h}$. This turns out to be too small to affect our results.

Let us now consider the contribution of intervalence absorption to the 5 ps peak. Since, as was previously shown, only a small fraction (7.8×10^{-4}) of the available valence electrons are excited by each pulse, within a few picoseconds the generated free holes scatter to the band maxima at $k = 0$. Consequently, the only possible intervalence transition is between the splitoff band (V_3) and the heavy hole band (V_2) for the 3.4 μm (0.37 eV) probe near $k = 0$. However, if we assume that the cross sections for two-photon absorption of 1.054 μm are the same for all three valence bands, then the tops of bands V_3 and V_2

are filled by holes to the same value of k. Consequently, absorption of 3.4 μm by the $V_3 \rightarrow V_2$ transition is not possible, and there is no contribution of intervalence absorption to the 5 ps peak.

The decay of the free-carrier peak at ~5 ps is not due to Auger recombination as was the case for Ge since $\tau_A = 3/\gamma N_e^2$ gives $\tau_A = 270\ \mu$s with $\gamma = 10^{-29}$ (GaAs value) [21] and $N_e = 3.3 \times 10^{16}/\text{cm}^3$. This does not compare to our observed values, <50 ps, which are also on the same order as the rate of decay of free carriers obtained by Tanaka [9] from photoluminescence. The mechanism for this rapid carrier relaxation has not been determined; however, its rapid decay agrees with present ideas on the reduction of carrier lifetimes by their capture by defects or impurities [22]. The rate is also too fast for radiative recombination (100–300 ps) [9], [10].

A remark should be made here concerning the two-photon absorption process assumed in the previous calculations. The theory of Bechtel and Smith for two-photon absorption [23] predicts that log $1/T$, where T is the percent transmission, is proportional to a slowly increasing function of excitation intensity (I) which is on the order of $I^{0.2-0.3}$ for the range of our experimental intensities. Our measurements of both the transmission of 1.054 μm and the induced IR absorption at the 5 and 192 ps peaks were independent of excitation intensity. The former is in agreement, within experimental error, with this two-photon absorption theory. Consequently, the major mechanism for the photogeneration of electron–hole pairs is by the simultaneous absorption of two 1.054 μm photons, and the induced IR absorption arises from processes involving these free carriers.

The appearance of a peak of induced absorbance delayed by 192 ps from the pump pulse for all three probe wavelengths suggested that impurity (defect) levels acting as traps for photogenerated carriers may be responsible for this absorption as well as that at 20 ps. In order to discuss this, we will consider the major impurity levels reported for similar samples of CdSe and shown in Fig. 6. Levels A and D were observed in a similar sample to that used in our experiments [24] and levels A' and D' were reported for other semi-insulating samples [25]. It can be seen from Fig. 6 that transitions $D \rightarrow D'$ are energetically possible for $\lambda_p = 3.4$ and 3.9 μm and $D \rightarrow C$, $A' \rightarrow D$, and $A \rightarrow A'$ for $\lambda_p = 2.2\ \mu$m. Since the 192 ps peak occurs for all three wavelengths, one may conjecture that the initial state for the absorptions corresponding to this delay is the D state. Consequently, the 20 ps peak may be due to $A' \rightarrow D$ or $A \rightarrow A'$. There is insufficient knowledge at this time on the dynamics of these states to explain the growth and decay of these peaks of induced absorption.

It should be mentioned that single-photon absorption of 1.054 μm is possible between the valence bands and the deep donor (D) at ~1.2–1.3 eV above the light hole band at $k = 0$ (see Fig. 6). This process has an absorption coefficient of ~0.5 cm^{-1} [24] and will populate this level with 1/5 of the free electrons generated by the two-photon process. This would somewhat reduce free electron absorption for all λ_p and possibly make a small contribution to absorption at 3.9 and 3.4 μm ($D \rightarrow D'$) and 2.2 μm ($D \rightarrow C$) for the 5 ps band (see Fig. 6).

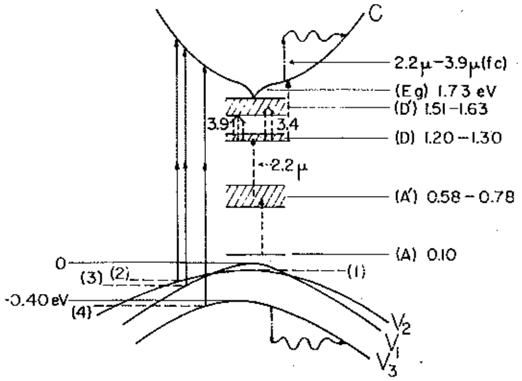

Fig. 6. Band structure near $k = 0$ for CdSe. Solid vertical lines indicate 1.054 μm excitation. The single dashed line represents the 2.2 μm probe, the double dashed, the 3.4 μm probe, the triple dashed, the 3.9 μm probe, and the dash dot, the 2.2 μm → 3.9 μm free-carrier probe (fc), with the wavy line representing phonon absorption and emission. The appropriate energies denoted by the dashed horizontal lines are (1) −0.024 eV, (2) −0.098 eV, (3) −0.15 eV, and (4) −0.46 eV. The effective masses are $m(C) = 0.13\ m_0$, $m(V_1)$, $m(V_3) = 0.45\ m_0$, and $m(V_2) = m_0$. The letters (A), (A'), (D), and (D') indicate possible impurity bands with their corresponding energies.

CONCLUSIONS

We would like to point out the usefulness of the pump and probe techniques using a tunable picosecond IR source to probe the dynamics of *free carriers* and *impurities* in semiconductors. This method is complementary to that of time-resolved photoluminescence which has been successfully used in studying these problems. By using sufficiently long probe wavelengths for Ge, we were able to eliminate contributions to induced absorption from indirect processes and effectively from intervalence transitions as well. This has clarified the dynamics of the remaining absorption process due to free carriers whose relaxation appears to be due to Auger recombination. For crystals of semi-insulating CdSe, the dynamics of the absorption process due to free carriers has also been identified without being able to explain its relaxation. We have made a plausibility argument to relate the appearance of two additional time-delayed absorption processes with transitions involving impurity (defect) states. The dynamics of these states remain to be understood. The techniques used in this study should be useful in obtaining information of importance in the application of semiconductors to very fast IR photodetectors and electronic devices.

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